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"RDGS" -

(Reduction of Defects in Germanium-Silicon)

Detached and Floating-Zone Growth of Semiconductor Crystals on the ISS

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ABSTRACT

Understanding the mechanism of detached Bridgman growth and establishing the growth of large scale germanium-silicon crystals by the float-zone technique are the key points of the project "RDGS – Reduction of Defects in Germanium-Silicon". The contact angle of the melt and the growth angle of the crystal are essential parameters which allow a controlled use of detached growth. The contact angle was determined for a variety of different substrates and melt compositions; pBN showed the highest value for pure germanium as well as for germanium-rich GeSi melts. The growth angle of $Ge_{0.95}Si_{0.05}$ was measured to be 8.5-10.5° which concurs with the values of pure germanium and silicon, respectively. The temperature dependence and the concentration dependence of the surface tension were determined for concentrations up to 10at% silicon ($\partial\gamma/\partial T=-0.08\cdot10^{-3}$N/m·K, $\partial\gamma/\partial C=2.2\cdot10^{-3}$N/m·at%). Using these values, the critical Marangoni number indicating the transition to time-dependent thermocapillary flow will be exceeded for the growth of large scale float-zone crystals onboard the ISS. Therefore, suitable tools for flow control are required.

INTRODUCTION

Detached growth of semiconductor crystals under microgravity conditions is one of the fascinating features observed in many space experiments (an excellent review is given in [1]) but its mechanism is neither completely understood nor can it be reproducibly obtained under earth conditions. Its benefits, however, are obvious: detached grown crystals show a strong reduction in the defect structure (e.g. etch pit density, small angle grain boundaries etc.) compared to crystals grown with wall contact [2]. The same (combined with a low impurity level) is valid for the crucible-free float-zone growth, but due to the hydrostatic pressure, floating-zone growth under earth conditions is normally restricted to small diameters. Only in space is it possible to obtain large size crystals [3, 4]. By understanding the mechanisms of detached growth in space through a series of controlled experiments, a transfer of this technique to earth conditions should be possible.

Germanium-silicon is a material system with a high potential for applications (x-ray and neutron optics, thermoelectric and photovoltaic devices, or, as thin films on silicon substrates, high frequency devices) but the lack of high quality bulk material is a severe drawback for wider use. Even for basic electrical and optical measurements, there is still an intense demand for high quality single crystals. The strong segregation, the high lattice mismatch, and the high reactivity of liquid silicon prevent the successful growth of single crystals with a low defect structure.

NASA, ESA, and the German DLR are supporting the present research program to investigate possibilities to reduce the defect structure in germanium-silicon either by achieving detached growth or by using the containerless float-zone technique (Fig. 1). It is a systematic investigation of the different parameters influencing detached growth, comparing the benefits or drawbacks of detached growth versus those of the complete wall-free floating-zone or the normal Bridgman technique. The experiments are planned for the Materials Science Laboratory (MSL) on the International Space Station (ISS). The detached Bridgman experiments will be performed in the LGF (Low Gradient Furnace), the floating-zone growth in the FMF (Floating Zone Furnace with Magnetic Field). The LGF is a multi-zone Bridgman furnace insert, its main specifications being a very high temperature stability (±0.01°C, controlled by sapphire fiber optics), a maximum temperature of 1500°C, and a hot core diameter of 30 mm. Flow control by rotating magnetic fields is possible. The FMF will be a seven-zone insert for zone melting or free melt zone processing, also with possible flow control by a rotating field. A special feature of the FMF will be the direct optical access into the hot core to observe and to control the position of the solid / liquid interface. Furthermore, it will be possible to investigate time-dependent growth processes in-situ by the application of the ultrasound pulse-echo method.

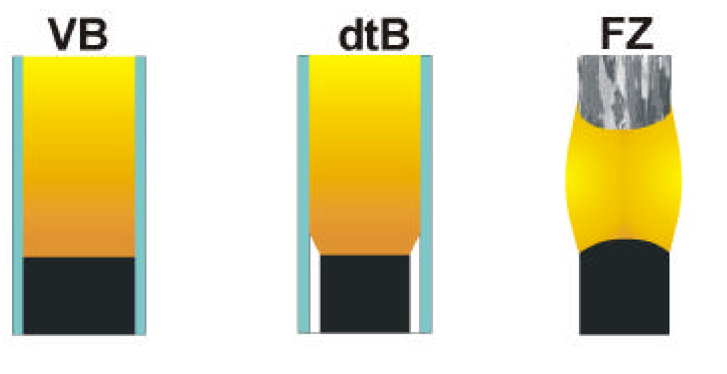

Fig. 1: Three different growth methods will be investigated with respect to defect formation and impurity levels in the system germanium-silicon: The normal Bridgman method, where the melt and the crystal are in contact with the crucible, the detached Bridgman method, where only the melt is in contact with the crucible, and the float-zone method, where neither the melt nor the crucible are in contact to a crucible.

GROWTH TECHNIQUES

This investigation involves the comparison of results achieved from three types of crystal growth of germanium-silicon alloys. The growth methods include Bridgman and float-zone, which are well-known, and detached Bridgman growth. Figure 1 depicts all three growth methods, figure 2 explains the details for the detached Bridgman method and the float-zone technique. In the case of normal Bridgman growth, the melt and the crystal are in contact to the crucible wall, in the case of detached Bridgman growth, only the melt is in contact, and for float-zone growth, neither melt nor crystal are in contact to the container wall. Comparing crystals grown by these three method with growth conditions as similar as possible, will answer the question of which defects are attributable to the container wall effects and which originate from other sources.

Detached Bridgman

First reports about detached growth (also called de-wetting or necking) are already more than 25 years old, as one of the results of the Skylab missions (e.g.: Yue and Voltmer with germanium in a graphite crucible [5], or Witt et al. with InSb in quartz-glass ampoules [6, 7]). In the intervening years, detached Bridgman growth has been observed in many microgravity experiments; good overviews of the substances and the crucible materials are given by Duffar et al. [8] and by Wilcox and Regel [1]. One of the most recent results was presented by Larson et al. [2] including an extensive characterization of partially detached growth of CdZnTe crystals (USML-1 and -2 missions) with regard to dislocation density, grain structure, transmittance, stress etc., demonstrating the positive influence of detachment on the quality of the grown crystals.

Although the mechanism of detached growth is not yet clear in all details, there is a common understanding about the main factors playing an important role in promoting detached growth:

- high contact angles between the melt and the crucible material / poor wetting of the crucible by the melt
- high growth angles
- gas pressure in the ampoule / pressure difference along the meniscus and between the gap and the top of the melt.
- reduced hydrostatic pressure.

Duffar et al. [9-13] pointed out that rough crucibles support de-wetting or at least reduce the melt area which is in contact with the crucible and lead therefore to reduced melt

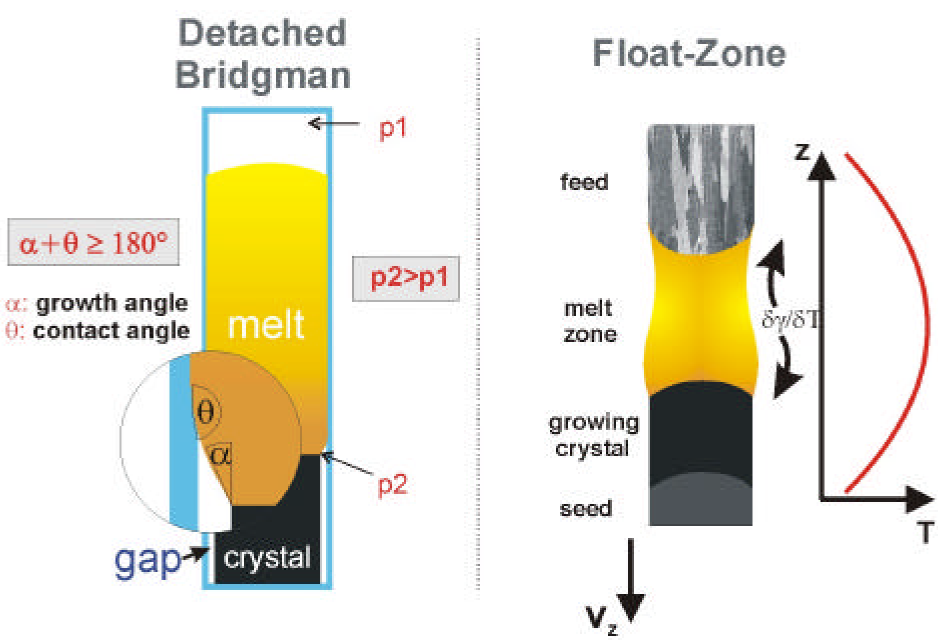

Fig. 2: Left: Detached Bridgman: A gap is formed if the sum of the growth angle á and the contact angle è is equal to or larger than 180°. The influence of a pressure difference between the gap (p2) and the top volume (p1) is under investigations.
Right: Float-zone: The melt zone is only hold by the surface tension of the molten material. Due to the temperature gradient toward the "cold" interfaces, thermocapillary flow develops.

contamination, but the remaining ampoule ridges in contact with the sample can give rise to secondary nucleation, twins, and grains.

According to Wilcox and Regel [14-18], detachment is supported or even initiated by the gas pressure due to the rejection of volatile impurities at the solid liquid interface and liberation of these impurities through the meniscus into the gap between crystal and ampoule. Another possibility to counterbalance the hydrostatic pressure was recently demonstrated by Duffar et al. [19]: detachment of GaSb was forced by active pressure control between the separated gas volumes at the top and the bottom of the melt. Nevertheless, under earth conditions it is not possible to achieve a pressure difference with a higher pressure in the gap than at the top because in this case bubbling will occur.

Float-zone growth

In the specific float-zone (FZ) growth method used here, a rod of material is supported on both ends and melted in a zone along the length of the rod by infrared radiation onto a localized, azimuthally symmetrical area of the surface. The liquid zone is held in place by surface tension. This zone is passed through the rod to grow a crystal. The advantages of FZ over Bridgman include the absence of a container in contact with the melt, which normally introduces impurities into the melt, and the absence of a container in contact with the processed crystal, which frequently causes stress-induced defects in the crystal because of the differential thermal contraction of the crystal and ampoule as they cool. The possibility to overcome the size limitation by processing under microgravity has been demonstrated in recent years with experiments on the space shuttle: Single crystals of GaAs with 20mm diameter and of GaSb with 16mm diameter, approximately three times the size of earth-grown float-zone crystals, have been successfully grown during these missions (STS 55/D2 in 1993 and STS 77/Spacehab-4 in 1996, respectively) [3, 4, 20]. A reduction of the etch pit density (EPD) by a factor of 5-8 has been found in microgravity GaAs crystals as compared to the Czochralski-grown starting materials [21], thus demonstrating the potential of containerless processing. Due to the large ratio of free surface to melt volume as compared to other melt growth processes, thermocapillary convection is dominant in all floating-zone experiments (excepting RF heating). For low Prandtl number melts, such as metals and semiconductors, the occurrence of dopant striations not generated by rotation or radio frequency heating, is practically always caused by time-dependent thermocapillary convection [22].

MEASUREMENTS OF MATERIAL PARAMETERS

The essential material parameters for detached growth are the contact or wetting angle between the melt and the crucible material and the growth angle of the crystal. In the case of float-zone growth, the temperature and the concentration dependence of the surface tension have to be known.

Contact (wetting) angle

Sessile drop measurements of Ge_xSi_{1-x} melts with compositions up to 13% Si have been performed. The sessile drop method is not free of contamination by the substrate, but it allows the parallel determination of surface tension and contact angle and actually resembles more closely the conditions of detached Bridgman crystal growth than contact-free methods such as electrostatic levitation.

The substrates used were square (25x25mm^2) plates of fused quartz, sapphire, pBN, AlN, glassy carbon coated graphite, SiC-coated SiC, ceramic Si_3N_4, and a CVD Si_3N_4 layer on fused quartz. The sample container was a horizontal fused quartz tube of 29mm inner diameter and a length of approximately 550mm, closed at one end by an optical window, open at the other end. The tube was placed in a tube furnace lined with a heat pipe of 3.5cm inner diameter to ensure isothermal conditions. In some runs, an additional carbon plate was placed behind the substrate on the substrate holder to act as oxygen getter. In each case, measurements were taken at different temperatures, usually in 10-20K intervals between the melting temperature and the maximum attainable temperature of 1090°C. In some of the runs, measurements were taken over several days to detect any slow reactions with the substrate or the atmosphere that might affect either the surface tension or the wetting angle.

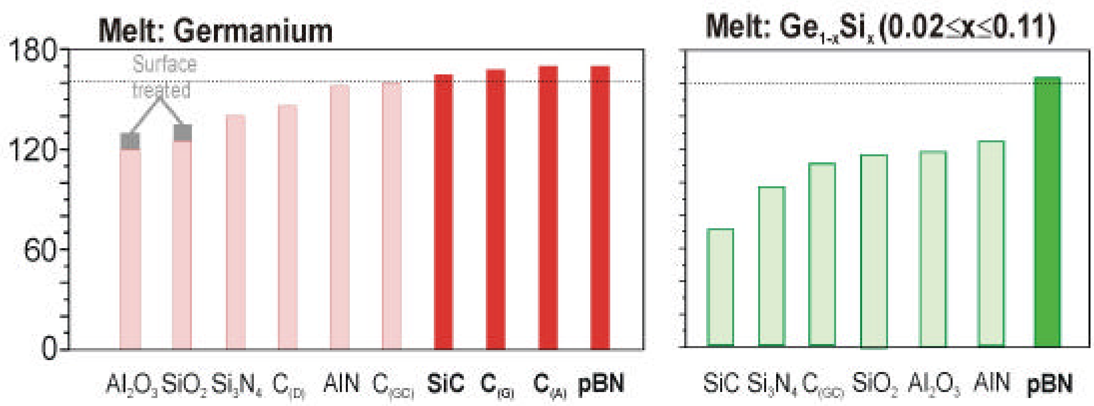

Fig. 3: Contact angle measurements for pure Ge (left hand side) and $Ge_{1-x}Si_x$ (x<0.13) (right hand side) on a variety of different substrates. Values higher than 160° (indicated by the dotted line) have been measured for SiC, graphite, carbon based aerogel, and pBN in the case of germanium. For GeSi, only pBN substrates gave contact angles higher than 160°.

A general result for the measurements of $Ge_{1-x}Si_x$ melts was that all the long-term measurements (3 days or longer) showed a reduction of the wetting angle over time. The rate of change was generally highest for the oxide substrates (SiO_2 and Al_2O_3) and slowest for pBN (a few degrees per day) and depended also on the surrounding atmosphere. This continuous reduction of the angle has one advantage, in that it can be assumed that all measured angles were advancing and not receding contact angles, the former being the one that is considered to be more reproducible and characteristic of the substrate surface properties.
The angles obtained under vacuum and under forming gas on pBN were the highest with values around 160°-170°, essentially the same as for pure Ge melts. The main results are summarized in Fig. 3, both for pure germanium melts as well as for GeSi melts.

Growth angle

The growth angle is defined as the angle between the meniscus surface and the growth direction of the crystal at the solid-liquid-gas trijunction (Fig. 4). Bardsley et al. [23] derived a dependence of the growth angle on the various interface energies from thermodynamic equilibrium considerations (see Fig. 4 for symbols):

$$a = \arccos\left(\frac{s_{sg}^2 + s_{\lg}^2 - s_{sl}^2}{2 \cdot s_{sg} \cdot s_{\lg}}\right)$$

Here, á is a material constant [1]. For small values of the interface curvature and the growth angle, and for the case that ó$_{sl}$«ó$_{lg}$, it can be derived that á=0 can only be fulfilled if the material is completely wetted by its melt (i.e. wetting angle è=180°). Most semiconductors and oxides, however, show incomplete wetting (e.g. è=30° for Ge and è=33° for Si [24] and hence á>0°. Unfortunately, the average growth angle has been measured only for a few materials.

The results of the measurements are summarized in Table 1 and in Figure 5.

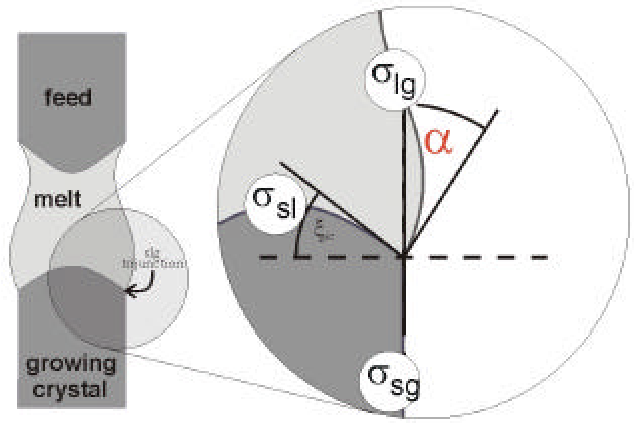

Fig. 4: Growth angle á. Important parameters controlling the floating zone process: ó$_{lg}$, ó$_{sl}$, and ó$_{sg}$ are the interface free energies liquid-gas, solid-liquid, and solid-gas, respectively.

The measurements for silicon and germanium are in good agreement with literature values (for detailed discussion of the literature see [25];) for germanium-silicon, no measurements are reported at all.

The measured value of germanium-silicon shows no remarkable deviation compared to the values for pure Si or Ge.

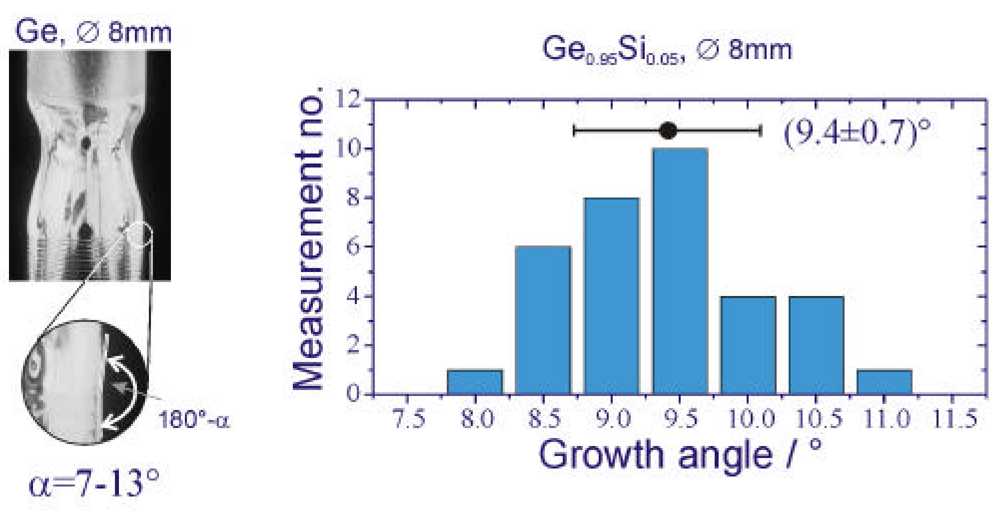

Fig. 5: Growing crystals by the float-zone method (left hand side), the growth angle á can be measured. For $Ge_{0.95}Si_{0.05}$, á was determined to 8.5 to 10.5°.

[1] In principle, the dependence of the growth angle on the growth geometry, the curvature of the solid-liquid interface, and the growth velocity has to be considered. For normal growth conditions, this might be neglected without introducing too large an error.

	Orientation	growth angle / °
Ge	<111>	7-13
$Ge_{1-x}Si_x$	<100>	8.5-10.5
Si	<100>	8-10

Table 1. Growth angles for germanium, silicon, and germanium-silicon.

Surface tension measurements

The surface tension of Ge_xSi_{1-x} melts was measured for compositions between x = 1 (pure Ge) and x = 0.886. The results are summarized in Figure 6. In contrast to the wetting angles, an asymptotic change of the surface tension over time was found only for two substrates: The ceramic Si_3N_4 substrate showed a definite effect (which could not be related to the processing atmosphere) with a reduction of about 10% within 8 hours. The glassy carbon substrate measurement also showed an asymptotic decrease of the surface tension, but to a much smaller degree, only by about 3%. With the exception of Si_3N_4, the measurements on glassy carbon resulted generally in smaller surface tension values than for the other substrates, in accordance with the results for pure Ge. This effect cannot be attributed to an effect as oxygen getter, since measurements on other substrates with a carbon plate behind the sample acting as getter did not show the reduced surface tension values.

The processing atmosphere, especially the use of argon or forming gas without any additional

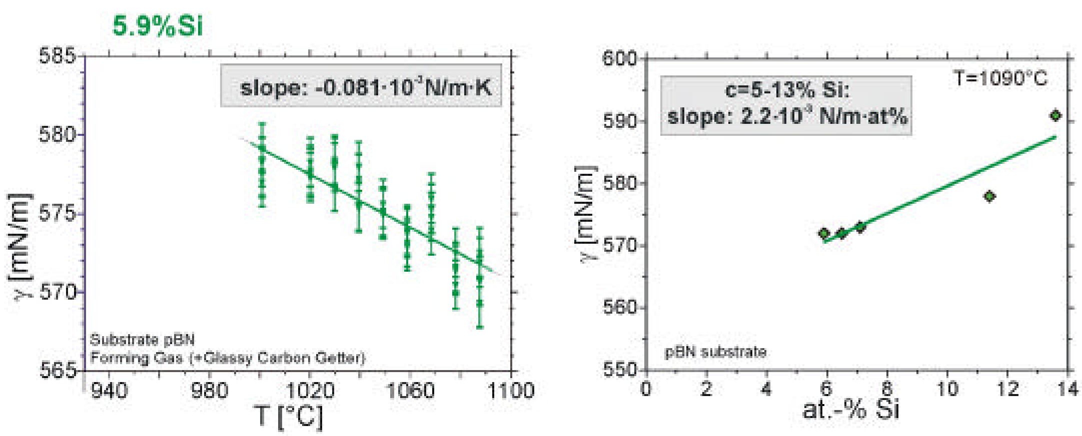

Fig. 6: Surface tension measurements for GeSi melts. The temperature dependence of the surface tension is shown on the left hand side, the concentration dependence on the right hand side.

oxygen getter, had an influence on the surface tension values; the effects were somewhat irreproducible and could be related to surface contamination. Going from dynamic vacuum to an argon atmosphere usually resulted in an increase of the apparent surface tension. This result is in agreement with the findings of Rhim [26] for Ge; his crucible-free measurements, done under dynamic vacuum resulted in a value of 583-0.08· (T-938°C). They are also lower than older literature values from measurements under an inert atmosphere and agree with the values measured in this work. Contamination effects also showed up in the temperature dependence of the surface tension, resulting in different coefficients for runs where the temperature was increased vs. runs where the temperature was decreased. The values shown in Figure 6 are those that showed reproducible values for the temperature dependence of the surface tension (from runs under vacuum or with carbon as an additional oxygen getter).

It should be noted that the surface tensions γ presented in Figure 6 are not the ones at the melting point, but have been normalized for a temperature of 1090°C. The concentration dependence was thus established by measuring γ and ∂γ/∂T for each composition, calculating γ for 1090°C from these results, and then determining ∂γ/∂C from this set of γ values.

CRYSTAL GROWTH EXPERIMENTS UNDER 1G

Detached Bridgman crystals

Several GeSi crystal growth experiments have been carried out in a LGF-like furnace under 1g conditions. Using pBN crucibles or pBN-tubes, partially detachment was observed in all of the crystals but none of them was grown completely detached. In all cases, germanium was used as seed material, the inner diameter of the samples was 12mm, the length of the crystals between 50 and 80mm. The growth velocity was 1mm/h, the temperature gradient at the solid-liquid interface was in the range of 40K/cm. The height difference between the attached and the detached grown areas has been determined by a profilometer: The gap width between

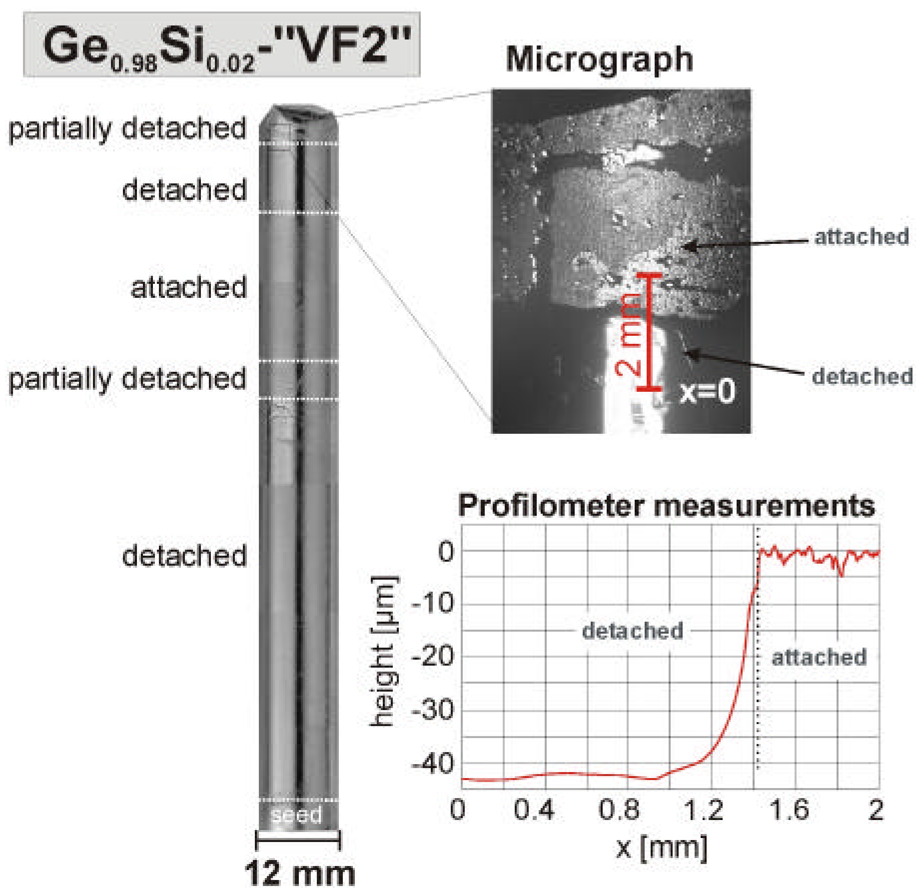

Fig. 7: GeSi crystal with an average silicon concentration of 2at%, grown partially detached under 1g conditions. The detached grown part can be distinguished by the reduced surface roughness and the shinier surface. In this case, the height difference (i.e. gap width) between the attached and detached grown area was 40µm.

the growing crystals and the container wall was in the range of a few micrometers up to about 100µm. As demonstrated in the sample in Fig. 7, a transition from attached to detached and back to attached was observed frequently, the cause for this behavior is under investigation.

Float-zone crystals

Using a monoellipsoid mirror furnace, single crystals with a maximum silicon concentration of 10at% could be grown reproducibly under 1g, but the diameter is limited to approximately 8mm. The growth was started with pure germanium, the silicon concentration was increased slowly using a pre-synthesized feed rod. Details about the growth results and the growth conditions will be given in [27]. The growth interface was stable up to a growth velocity of 1mm/h. Upon exceeding this threshold value, morphological instabilities occurred. Above a certain silicon concentration, the interface was irregularly bent (Fig.8). Theoretical considerations based on the coefficient of the concentration dependence of the surface tension as well as numerical simulation of the flow and the concentration field point out that these irregularities can be attributed to solutocapillary convection. The high value of $\partial\gamma/\partial C$ and the high segregation coefficient of silicon in germanium (k_0 5 for germanium -rich GeSi melts) generate a strong solutocapillary flow in front of the solid-liquid interface.

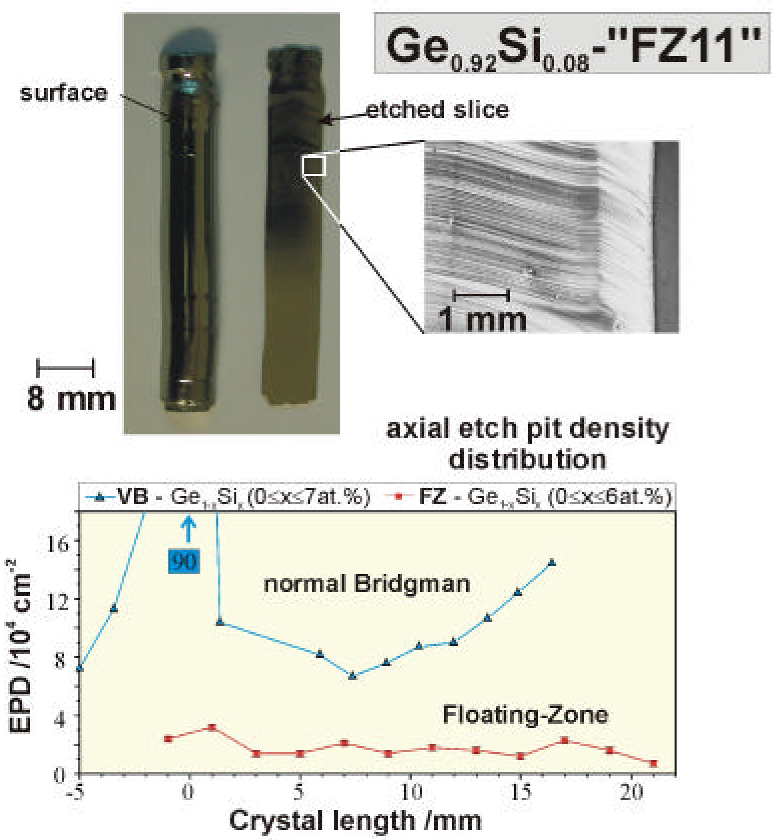

Fig. 8: GeSi crystal with a maximum silicon concentration of 8at%, grown by the float zone method under 1g. The hydrostatic pressure limits the crystal size to 8mm in diameter (upper left hand side). The micrograph image of an etched axial slice shows an irregular interface curvature which can be attributed to solutocapillary convection. The EPD of the float zone crystal is considerably reduced compared to a crystal grown by the normal Bridgman method.

SUMMARY

The project “RDGS – Reduction of Defects in Germanium-Silicon” is an international cooperation supported by NASA, ESA, and the German DLR to perform detached Bridgman and float-zone experiments on board of the ISS. The detachment is strongly influenced by the contact (or wetting) angle of the material and the growth angle of the growing crystal. Consequently, these values have been investigated for a variety of different experimental conditions. For float-zone growth, the temperature and concentration dependence of the surface tension are the crucial parameters. Using the sessile drop method, these values have been determined for the interesting temperature and concentration range.

Due to the knowledge of those material and process parameters, we are now able to obtain partially detached GeSi crystals under 1g as well as small-scale float-zone GeSi crystals.

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